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IS 1039 (1989): Textiles - Estimation of small quantities of copper, iron, manganese, chromium and zinc [TXD 5: Chemical Methods of Test]

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IS 1039 : 1989
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Indian Standard

TEXTILES — ESTIMATION OF SMALL QUANTITIES OF COPPER, IRON, MANGANESE, CHROMIUM AND ZINC

(First Revision)

भारतीय मानक

वस्त्रादि — ताम्बा, लोहा, मेंगनीज, क्रोमियम और जस्ता को अल्प मात्राओं को ज्ञात करना

(पहला पुनरीक्षण)

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Chemical Methods of Test Sectional Committee, TDC 5

FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards on 15 May 1989, after the draft finalized by the Chemical Methods of Test Sectional Committee had been approved by the Textile Division Council.

This standard was first published in 1956. It has been now revised to make it up-to-date on the basis of experience gained during its use. In this revision, the following modifications have been carried out:

a) Since the methods are applicable to all textiles, namely treated, untreated and proofed, the title and scope have been modified accordingly.

b) The methods of test for estimation of small quantities of copper, iron, manganese, chromium and zinc have been modified according to the latest developments to include spectrophotometric determination. In the revised methods, details have been prescribed for destruction of organic matter by wet or dry ashing, removal of interfering ions, and procedure in a systematic manner.

Even when present in small quantities, rubberized, oil-coated or similarly proofed cotton fabrics (or in basic fabric intended to be proofed) metals, such as copper, iron, manganese, chromium and zinc tender the fabric on reaction with cellulose or otherwise deteriorate it. The formulation of standard methods for estimation of small quantities of these metals in basic and proofed cotton cloth are, therefore, necessary.

The methods prescribed in this standard are applicable in estimating metals when present individually or in combination with others. Every precaution should be taken to protect the fabric being sampled, the samples and the apparatus and reagents used, from adventitious contamination both before and during the test and chemicals of the analytical reagents grade and absolutely clean apparatus should be used.

The accuracy of the methods prescribed depends to a large extent on the ability of analyst and use of pure chemicals. The methods are suitable for fully trained analysts only.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

TEXTILES — ESTIMATION OF SMALL QUANTITIES OF COPPER, IRON, MANGANESE, CHROMIUM AND ZINC

(First Revision)

1 SCOPE

1.1 This standard prescribes methods for the estimation of small quantities of copper, iron, manganese, chromium and zinc in all kinds of textiles.

1.2 The methods of test prescribed in this standard are applicable only if the total quantity of all the metals present does not exceed 0·2 percent (*m/v*) in any one of the test solutions or suspensions.

2 REFERENCES

2.1 The following Indian Standards are necessary adjuncts to this standard.

IS No.	*Title*
IS 199 : 1989	Methods for estimation of moisture, total size or finish, ash and fatty matter in grey and finished cotton textile materials (*third revision*).
IS 1070 : 1977	Specification for water for general laboratory use (*second revision*).

3 SAMPLING

3.1 The sample from the lot shall be drawn so as to be representative of the lot. Sample drawn in accordance with the procedure specified in relevant material specification or as agreed to between the buyer and the seller shall be taken as representative of the lot.

4 PREPARATION OF TEST SPECIMEN

4.1 The test sample shall be constituted of pieces or swatches of approximately one square metre. From each such swatch, four test specimens, 7·5 cm × 7·5 cm each, shall be cut out from random locations. All the test specimens shall then be shredded into fine fragments and mixed thoroughly.

5. APPARATUS

5.1 Flat Bottomed Conical Flasks with Neck Extensions — of 150 ml or 250 ml capacity.

5.2 Sintered Porcelain Crucibles — of appropriate capacity.

5.3 A Muffle Furnace

5.4 Spectrophotometer or Spekker Absorptiometer or Colorimeter.

5.5 Hot Plate — with provision for maintaining graded surface temperatures.

5.6 Safety Glass Screen

5.7 Boiling Rods — made by rotating suitable lengths of 5 mm diameter glass tubing in a small flame impinging about 10 mm from one end, until the wall at that point is completely fused leaving a small cup beyond. This cup is immersed in the liquid when the rod is in use.

6 QUALITY OF REAGENTS

6.1 Unless specified otherwise, pure chemicals shall be employed in tests and distilled water (IS 1070 : 1977) shall be used where the use of water as a reagent is intended.

NOTE — 'Pure chemicals' shall mean chemicals that do not contain impurities which affect the test results.

7 ESTIMATION OF COPPER (Cu)

7.1 Destruction of the Organic Matter

7.1.1 *Method 1 — Wet Ashing*

This method is preferable to Method 2, particularly when the amount of copper is very small, or when substances containing silicon (for example, china clay) are present. Prepare wet ash of the test specimen by the method prescribed in Annex A. Also prepare a 'blank' by evaporating appropriate quantities of the acids to about the same volume as that of the residue from the combustion. Take particular care to expel chlorine completely from both solutions.

7.1.2 *Method 2 — Dry Ashing*

Determine the mass of the test specimen before ashing, place in a porcelain crucible and impregnate with 5 percent solution of magnesium nitrate at the rate of 1 ml per gram of the test specimen. Alcohol may be used to facilitate the impregnation of grey cotton or poorly wettable materials. Take care to ensure that the inner surfaces of the crucible have not been damaged or roughened as this may lead to loss of copper by combination with the glaze. Prepare dry ash of the test specimen as prescribed in IS 199 : 1989 and dissolve the ash by heating on a water-bath with 5 ml of 2 N sulphuric acid and prepare a 'blank' by mixing 5 ml of the same acid with the appropriate quantity of magnesium nitrate.

7.2 Selection of Method

7.2.1 The dithizone method (Method B) is more sensitive, but the choice depends largely upon the amount and nature of other substances present; the effects of different extraneous ions are summarized in Table 1. The amounts given in col 2 are the largest considered likely to be derived from a 2-g sample of the material. The expression 'no interference' in col 3 and 4 signifies that at least this amount of the ion in question may be tolerated. Interactions between different extraneous ions are not considered.

7.3 *Determination*

7.3.1 *Method A* — With sodium diethyldithiocarbamate.

7.3.1.1 *Reagents*

a) *Sodium diethyldithiocarbamate 0·2 percent solution*

This solution is best prepared in small quantities at weekly intervals and should be filtered before use.

b) *Ammonium citrate 20 percent solution*

Dissolve 16 g citric acid in water and add ammonium hydroxide solution (relative density 0·880) until the solution is just acid to litmus paper. Dilute the cooled solution to 100-ml and shake it in a separating funnel with a small amount of an approximately 0·01 percent solution of dithizone in carbon tetrachloride, further quantities of this being added, if necessary, until the solvent layer remains green, blue or violet after the mixture has been shaken vigorously for 2 minutes. Separate the solvent layer and shake the aqueous layer with successive small amounts of purified carbon tetrachloride (*see* below) until the solvent remains colourless. Filter the reagent to remove droplets of the solvent.

c) *Carbon tetrachloride*

Fresh supplies of the solvent may contain carbon disulphide and should be purified as follows:

Add alcoholic potassium hydroxide solution, with shaking, until no further yellow colour develops. Allow the mixture to stand for 1 hour, wash it several times with water and treat as described below.

Used carbon tetrachloride that has accumulated from previous analysis, or new solvent that has been partly purified as above, shall be shaken with successive portions of concentrated sulphuric acid until the acid layer remains colourless. Then shake the solvent with powdered calcium hydroxide until evaporation of a test sample on litmus paper shows that it is free from acid. Finally filter it through Whatman filter paper No. 1 and distil it.

7.3.1.2 *Procedure*

Place 10 ml of ammonium citrate solution and a few drops of phenolphthalein indicator in a 100-ml separating funnel, add the ash solution (*see* **7.1**) or a suitable aliquot containing not more than 150 µg of copper, and dilute the mixture to about 30 ml with water. Gradually run in ammonium hydroxide solution of any convenient strength until a permanent faint pink colour is obtained, cool the solution and add 2 ml of sodium diethyldithiocarbamate solution. Extract the brown precipitate by shaking with 20 ml of carbon tetrachloride.

If the presence of lead, mercuric, zinc or zirconium ions is suspected, add further quantities of sodium diethldithiocarbamate solution at this point until the depth of colour of the carbon tetrachloride layer no longer increases. Add small amounts of the reagent in the two subsequent extractions to ensure that all the copper has reacted. Do not carry out the extractions in strong day light and shield the extracts from light whenever possible.

Run the lower (solvent) layer into a 50-ml graduated flask and re-extract the aqueous layer with two successive portions (each 10 ml) of carbon tetrachloride, the second of which should remain colourless. Dilute the combined solvent extracts to 50 ml with carbon tetrachloride and dry by shaking with 1 g of anhydrous sodium sulphate. The solution is stable for at least 24 hours unless exposed to strong daylight. Treat the 'blank' solution prepared as described in **7.1**, or an aliqout portion corresponding to that used for the actual test, exactly as described above.

Decant the dry solutions into the 1 cm or 4 cm cells of a Spekker absorptiometer and measure their optical densities with the use of Ilford 601 violet filters. Maximum absorption occurs at a wavelength of approximately 440 nm. Obtain the copper contents from a calibration graph in which the optical densities of extracts prepared as above from aqueous solutions

Table 1 Effects of Extraneous Ions

(*Clause* 7.2.1)

Extraneous Ion	Amount mg	Sodium Diethyldithiocarbamate (Method A)	Dithizone (Method B)
(1)	(2)	(3)	(4)
Aluminium	15	No interference	No interference
Antimonous	150	No interference	No interference
Antimonic	150	No interference	Interferes at all concentrations (*see* Note 1)
Borate	100	No interference	No interference
Calcium	50	No interference	No interference
Chromic	75	Interferes at concentrations above 1 mg chromium (*see* Note 2)	No interference
Chromate	75	No interference	Interferes at all concentrations (*see* Note 1)
Cobaltous	1	Interferes at all concentrations	No interference
Ferric	25	No interference	Interferes at concentrations above 20 mg iron (*see* Note 3)
Lead	15	More reagent A1* required	No interference
Magnesium	20	No interference	No interference
Manganous	15	Interferes at concentrations above 1 mg manganese (*see* Note 4)	No interference
Mercuric	5	More reagent A1* required	Interferes at all concentrations
Phosphate	500	No interference	No interference
Sodium	30	No interference	No interference
Stannic	500	Interferes at concentrations above 5 mg tin (*see* Note 2)	Interferes at concentrations above 5 mg tin (*see* Note 5)
Titanium	40	No interference	Interferes at concentrations above 10 mg titanium (*see* Note 5)
Zinc	80	More reagent A1* required	No interference
Zirconium	15	More reagent A1* required	No interference (*see* Note 5)

*Sodium diethyldithiocarbamate (0·2 percent).

NOTES

1 Reagents destroyed by oxidation.

2 Hydroxides of the extraneous ions are precipitated and difficulties arise if the amount of the precipitate is too large.

3 Amounts of ferric iron up to 25 mg may be present if 4 ml of the buffer solution is used [*see* **7.3.2.1** (b)].

4 Amounts of manganese between 5 mg and 15 mg give the extract a pink colour. Within this range the absorption varies little with the manganese content and is about the same as that produced by 3 µg of copper.

5 Phosphates of the extraneous ions are precipitated and difficulties arise if the amount of the precipitate is too large.

containing different known amounts of copper are plotted against the copper contents of the corresponding aqueous solutions. Prepare the latter by suitably diluting a more concentrated solution of copper sulphate.

Any other absorptiometer or colorimeter may be used, or the colours of the extracts may be compared visually, in tubes of uniform dimensions, with those of a series of extracts freshly prepared from solutions of known copper cotent. These alternatives may, however, affect the maximum permissible amount of copper in the solution taken for extraction.

7.3.2 *Method B* — With diphenylthiocarbazone (dithizone).

7.3.2.1 *Reagents*

a) *Dithizone, 0·002 percent solution in purified carbon tetrachloride* — Prepare the solution daily and purify as follows:

   Shake 10 ml of a 0·02 percent stock solution of dithizone in purified carbon tetrachloride in a separating funnel with 20 ml of water containing a drop of dilute ammonium hydroxide solution. Reject the yellowish-brown solvent layer and shake the aqueous layer with a small amount of carbon tetrachloride, which is also rejected. Add 100 ml of carbon tetrachloride and then sufficient dilute hydrochloric acid to precipitate all the dithizone from the aqueous layer. Dissolve the precipitate in the solvent by shaking and run the solution off through a plug of loose cotton wool inserted in the stem of the funnel to remove droplets of water.

   If stored in a stoppered vessel in a cool, dark place the reagent is sufficiently stable for one day's work. Under similar conditions the 0·02 percent stock solution may be kept for about a week.

b) *Buffier solution*

   Dissolve 75 g citric acid and 19 g anhydrous sodium dihydrogen phosphate in water. Dilute the mixed solution to 250 ml and purify it exactly as described for the ammonium citrate solution.

c) *Tropaeolin 00, 0·1 percent aqueous solution*

   Dissolve 0·1 g of the solid in 100 ml of water.

7.3.2.2 *Procedure*

Place 2 ml of the buffer solution in a 50 ml separating, funnel add the ash solution (*see* **7.1**) or a suitable aliquot containing not more than 10 µg of copper, and dilute the mixture to about 20 ml with water. Add ammonium hydroxide solution (relative density 0·880) gradually until the mid hue of the indicator is reached, cool the solution and add 10·0 ml of dithizone solution by means of a pipette. Shake the funnel steadily for 2 minutes (about 240 strokes). The colour of the lower (solvent) layer should now be green, blue or violet. If it is violet-red add a further quantity (10·0 ml) of dithizone solution and repeat the shaking.

Run the solvent layer into another separating funnel and shake for 30 seconds with 10 ml of 0·1 N hydrochloric acid (*see* Note 1). If it is then still red reject it and repeat the determination with a smaller aliquot of the original solution. Otherwise, draw it off through a small tuft of cotton wool inserted in the stem of the funnel to remove droplets of water and collect it in a 1 cm cell of the Spekker absorptiometer. Treat the 'blank' solution, prepared as described in **7.1**, or an aliquot portion corresponding to that used for the actual determination exactly as described above.

Measure the optical densities of the extracts with the use of green filters. Maximum absorption of the copper complex occurs at about 550 nm, but it is preferable to make measurements at 510 nm where the absorption of the unchanged dithizone is at a minimum. The difference between the optical densities of the 'test' and 'blank' extracts is used to obtain the copper content directly from a calibration graph constructed as follows.

Extract a series of solutions containing different measured amounts of a standard solution of copper sulphate as above and measure the optical densities of the extracts. Subtracts from each value the optical density of the extract from a similar solution containing no added copper and plot the differences against the copper contents of the original solutions. These differences are substantially independent of the concentration of the dithizone solution within the range 0·001 5 percent to 0·002 5 percent.

Any other absorptiometer may be used, or the colour of the extract and those of extracts prepared similarly from a series of aqueous solutions containing known amounts of copper may be compared visually in small stoppered tubes of uniform dimensions. It is not possible to make the comparison in colorimeters of the Duboseq type. The colours are stable for few hours if the solutions are protected from light.

NOTES

1 If zinc is known to be absent, or if the amount present is less than about 1 mg, the acid wash may be omitted. Zinc tends to react more rapidly than copper and when large amounts of zinc are present, the solvent layer may become bright red. Copper is extracted completely, however, by a solution of the zinc complex, the copper complex being unaffected by the acid wash which removes the zinc from the solvent layer.

2 The success of this method depends on scrupulous cleanliness. All apparatus shall be washed, first with dilute hydrochloric acid and then with distilled water immediately before use.

8 ESTIMATION OF IRON (Fe)

8.1 Destruction of the Organic Matter

8.1.1 *Method 1 — Wet Ashing*

Follow the procedure described in **7.1.1**. This method is preferable to Method 2 particularly when the amount of iron is small or when siliceous substances are present.

8.1.2 *Method 2 — Dry Ashing*

Determine the mass of the test specimens before ashing, place in a porcelain crucible and impregnate with a 5 percent solution of magnesium nitrate at the rate of 1 ml per gram of test specimen. Alcohol may be used to facilitate the impregnation of poorly wettable materials. Take care to ensure that the inner surface of the crucible has not been damaged or roughened, as this may lead to loss of iron by combination with the glaze. Prepare dry ash by the method prescribed in IS 199 : 1989 and dissolve the ash by treating it with 1 ml of concentrated hydrochloric acid and evaporate to dryness on a water-bath; dissolve the residue in dilute hydrochloric acid. Prepare a 'blank' by evaporating 1 ml of concentrated hydrochloric acid with the appropriate quantity of magnesium nitrate solution.

8.2 Selection of Colorimetric Method

8.2.1 The mercaptoacetate method (Method A) is relatively simple, but is limited in its application by the interference of certain other ions, as shown in Table 2. The oxine method (Method B) is more tedious, but may be applied in presence of nearly all the ions shown in the table without preliminary separations. It is also slightly more sensitive than the mercaptoacetate method.

The amounts given in col 2 of the Table 2 are the largest likely to be derived from a 2 g sample of the material; the expression 'None' in col 3 and 4 signifies that at least this amount of the ion in question may be tolerated under the conditions set out in **8.3.1** and **8.3.2**. Interactions between different extraneous ions are not considered.

8.3 Determination

8.3.1 *Method A* — With mercaptoacetic acid.

8.3.1.1 *Reagents*

a) *Mercaptoacetic acid*, 10 percent

b) *Ammonium chloride or ammonium sulphate*, free from iron.

If a suitably iron free sample is not available a 20 percent *m*/*v* solution may be purified as follows.

Treat the solution with oxine solution until an excess appears to be present (1 ml to 2 ml is usually sufficient) and adjust with dilute ammonium hydroxide until just acid to litmus paper. Extract the solution with successive portions of chloroform until the extract is colourless and finally filter it to remove suspended solvent.

8.3.1.2 *Procedure*

Transfer the acid solution from the ashing procedure, or an aliquot containing not more than 200 μg of iron, to a 50 ml volumetric flask. Add ammonium chloride or ammonium sulphate so that the amount of ammonium salts finally present in the neutralized solution will be 3 to 5 g. Add 1 ml mercaptoacetic acid solution, followed by ammonium hydroxide solution (relative density 0·880) until a red colour develops. Add a further 1 ml of ammonium hydroxide. Cool the solution and dilute to 50 ml. It is stable for at least 2 hours if free from copper.

Treat the 'blank' solution, prepared as described in **8.1**, or an aliquot portion corresponding to that used for the actual determination exactly as described above.

Decant the solutions into 4 cm cells of the Spekker absorptiometer and measure their optical densities with the use of Ilford 604 green filters. Maximum absorption occurs at a wavelength of approximately 530 nm. Obtain the iron contents by reference to a graph, in which the optical densities of standards prepared as above from solutions containing known amounts of iron are plotted against their iron contents. The standards may be prepared by dilution of a solution of ferric alum in 0·1 N sulphuric acid.

Any other absorptiometer or colorimeter may be used, or the samples may be compared visually with freshly prepared standards in tubes of uniform dimensions. These variations may, however, affect the maximum permissible amount of iron in the solution.

8.3.2 *Method B* — With 8-hydroxyquinoline (oxine).

8.3.2.1 *Reagents*

a) *Sodium tartrate 2M* — Free a solution containing 460 g of the hydrated salt per litre from iron as described for reagent in **8.3.1.1** (b).

b) *Ammonium chloracetate 4M* — Dissolve chloracetic acid (380 g) in water and neutralize with ammonium hydroxide (relative density 0·880) the solution being cooled during the process to reduce hydrolysis. Free the solution from iron as described above for reagent in **8.3.1.1** (b).

c) *Oxine, 5 percent solution in 2M acetic acid.*

d) *Potassium cyanide buffer* — Prepare the solution, which has a *p*H value of 8·5 by dissolving 0·5 g of potassium cyanide in 100 ml of 0·06 N hydrochloric acid. Store this in well stoppered bottles and reject it if it becomes discoloured.

Table 2 Effects of Extraneous Ions

(*Clause* 8.2.1)

Extraneous Ion	Amount (mg)	Mercaptoacetate (Method A) Interference	Oxine (Method B) Interference
(1)	(2)	(3)	(4)
Aluminium	15	None up to 1 mg*	None with slightly modified mothod (*see* Note 1)
Antimonic	150	None up to 25 mg*	None
Antimonous	150	None up to 40 mg*	None
Borate	100 of H_3BO_3	None	None
Calcium	50	None	None
Chromic	75	Slight at 0·1 mg*	None with slightly modified method (*see* Note 1)
Cobaltous	1	None up to μg†	None
Cupric	35	Amounts greater than 10 μg cause fading	Upper light 3 mg (*see* Note 2)
Lead	15	Amounts greater than 10 mg cause high results	None
Magnesium	20	None	None
Manganous	15	None	None
Mercuric	5	None	None
Molybdate	1 000 of Mo	None up to 1 mg†	Negligible up to 20 mg Mo
Phosphate	500 of H_3PO_4	Recovery about 99 percent at 500 mg	None
Sodium	30	None	None
Stannic	500	None up to 15 mg*	None up to 100 mg by modified method (*see* Note 3)
Titanic	40	Slight at 0·1 mg*	None by modified method (*see* Note 3)
Tungstate	1 000 of W	None up to 10 mg†	None up to 100 mg
Vanadate	1 000 of V	None up to 1 mg†	Interferes at all concentration
Zinc	80	None	None
Zirconyl	15 of Zr	Slight at 0·1 mg*	Retards extraction of iron (*see* Note 4)

*These ions interfere because they form insoluble hydroxides. It should be noted that many of them for m complexes with mercaptoacetic acid and when large amounts are present; this may result in bieaching of the colour of the iron complex Clarity of the solution is not, therefore, a trustworthy indication of non-interference. The amounts quoted are the largest with which quantitative recovery of iron may be obtained.

†These ions interfere by forming coloured complexes with the reagent.

NOTES

1 When aluminium or chromium is present, low results are obtained if much heat is developed during the preliminary neutralization in presence of tartrate. In this case, the solution is roughly neutralized with ammonium hydroxide, acidified with 5 ml of sulphuric acid, and cooled before the sodium tartrate is added.

2 Copper oxinate is normally extracted along with the iron and separated by washing with the cyanide buffer solution. If the amount of copper exceeds 3 mg, however, the precipitated oxinate will not dissolve completely in chloroform and the recovery of iron may be low.

(*Continued*)

Table 2 Effects of Extraneous Ions — *Contd*

3 If tin or titanium is present the ash solution shall be kept strongly acid and not be diluted until immediately before the analysis. Otherwise, hydrolysis may cause the chloroform layer to emulsify, even through no visible precipitate is present. If more than 10 mg of the metals is present, a portion will be extracted as oxinate and appear in the chloroform layer. In this case the first extract is run, without filtration, into a separating funnel containing 50 ml of 0·1 N sulphuric acid, and shaken until the solvent layer becomes colourless. 1 ml of sodium tartrate solution, 1 ml of oxine solution, and 3 ml of ammonium chloracetate solution are added to the contents of the funnel which is then shaken for 1 minute. Only the oxinates of iron and copper return to the solvent layer which is then drained into potassium cyanide solution as above.

4 The zirconyl ion causes low results if heat is developed in the preliminary neutralization in presence of tartrate. It is also too readily hydrolysed to enable the modification described for aluminium or chromium to be employed. Further, it appears to retard the extraction of iron. If it is desired to avoid separating this ion, recoveries of iron of the order of 95 percent may be obtained by adding ice to the solution before the preliminary neutralization and by shaking with the chloroform for 5 minutes.

e) *Chloroform* — This may be recovered by shaking first with successive portions of concentrated sulphuric acid until the acid layer remains almost colourless, then with an excess of calcium hydroxide, filtering and finally distilling. Add alcohol at the rate of 1 percent by volume to the distillate.

f) *Methyl orange*, 0·1 percent.

8.3.2.2 *Procedure*

Transfer the acid solution from the ashing procedure, or an aliquot portion containing not more than 250 µg of iron, to a 250 ml conical flask and dilute to 30 ml. Cover the flask by a light shield (*see* Note 2). Add 1 ml sodium tartrate solution and a few drops of methyl orange indicator and neutralize the solution with concentrated ammonium hydroxide solution. The end point is easily observed, without removal of the shield, by holding the flask a short distance above a white tile and looking down the neck. Cool the flask rapidly in running water, the shield being removed temporarily and exposure to strong daylight avoided; make any necessary adjustment of the *p*H with dilute acid or alkali. Add 2·5 ml 2N sulphuric acid, 1·0 ml oxine solution and 3·0 ml ammonium chloracetate solution in that order with intermediate mixing, the solution being transferred to a 100 ml separating funnel and diluted to about 50 ml. Add 25·0 ml chloroform and shake the contents of the funnel steadily for 2 minutes (about 300 cycles).

Drain the solvent layer through a tuft of cotton wool inserted in the stem of the funnel and collect it in another 100 ml separating funnel containing 20 ml of potassium cyanide solution. Shake this funnel for 1 minute and drain the solvent layer through another cotton plug directly into a cell of the Spekker absorptiometer. Measure its optical density with the use of Ilford No. 602 blue filters, maximum absorption being at about 470 mm. The extract is stable for at least 1 hour if evaporation is prevented.

Treat the 'blank' solution, prepared as in **8.1**, or an aliquot corresponding to that used for the actual determination, exactly as above.

Determine the iron content by reference to a calibration graph prepared as follows.

Dilute measured amounts of a standard solution of ferric alum in 0·1 N sulphuric acid with water to 50 ml and treat as described above, omitting neutralization to methyl orange. If a freshly prepared solution of oxine is used, the 'blank' should show only a very small absorption which is calculated as iron by assuming the graph near the origin to be linear. Add this amount of iron to each standard when the graph is plotted and extrapolate the curve to the origin. Any other absorptiometer may be used, or the extracts may be compared visually with freshly prepared standards in tubes of similar dimensions. These variations may, however, affect the maximum amount of iron that may be present.

NOTES

1 All apparatus should be rinsed with dilute hydrochloric acid and then with water before use. Care should be taken that no acid remains round the stopcocks of separating funnels, and unbuffered solutions should not be placed in the funnels.

2 Ferric ions in faintly acid solution containing tartrate are reduced by light. Suitable light shields in the form of truncated cones may be made from black paper They should cover the sides of the flask completely and should be loose enough to project about 2 cm below the base when the flask is lifted. After tartrate has been added the shields should not be removed (except for the brief interval while the flask is cooled) until the chloracetate has been added.

9 ESTIMATION OF MANGANESE (Mn)

9.1 Destruction of the Organic Matter

9.1.1 *Method 1 — Wet Ashing*

This method is preferable to Method 2, particularly when siliceous substances are present. Follow the procedure described in Annex A and prepare a 'blank' by evaporating appropriate quantities of the acids to about the same volume as that of the residue from the combustions. Add 0·1 ml of 5 percent sodium sulphite solution to the diluted residues before they are boiled to expel chlorine. This dissolves traces of manganese dioxide formed during the reaction. Filter off any silica or lead sulphate before proceeding with the analysis.

9.1.2 *Method 2 — Dry Ashing*

Use crucibles, preferably porcelain, which have not become roughened on the inner surface and, before igniting, impregnate the sample with a 5 percent solution of magnesium nitrate [$Mg(NO_3)_2.7H_2O$] at the rate of 1 ml/g. If necessary, use alcohol to assist penetration. These precautions reduce the possibility of loss of manganese by combination with the glaze of the crucible. Ash the sample as described in IS 199 : 1989. Dissolve the ash by heating it with 1 ml to 2 ml of concentrated hydrochloric acid, add 2 ml of 1 : 1 sulphuric acid solution, evaporate and, in order to expel chlorides, heat until fumes of sulphuric acid are evolved. If Method B is to be used the hydrochloric acid solution may be used directly. Filter off any silica or lead sulphate before proceeding with the analysis. Prepare a blank by evaporating to fuming point a mixture of the appropriate quantities of magnesium nitrate solution, concentrated hydrochloric acid and 1 : 1 sulphuric acid.

9.2 Selection of Method

9.2.1 The formaldoxime method (Method B) is about five times as sensitive as the periodate method (Method A), but the latter is some what simpler. The choice may be governed by the amount and nature of other substances present. The maximum amounts of various ions that are likely to be derived from a 2 g sample of textile material are given in Table 3. The effects of these ions on the two methods under the conditions detailed in **9.3** are summarized in col 3 and 4, the expression 'No interference' signifying that at least the stated amount of the ion in question may be tolerated.

9.3 Determination

9.3.1 *Method A — With Potassium Periodate*

Remove any interfering ions as detailed in the Notes and place the prepared sample solution or an aliquot containing not more than 400 µg of manganese in a 100 ml conical flask. Add sulphuric acid until a total volume of 6 ml of concentrated acid is present and dilute to about 40 ml with water. Add 0·25 g of potassium metaperiodate (KIO_4), heat the solution to boiling and keep it at, or preferably slightly below, the boiling point for 1 hour keep the flask covered in order to minimize evaporation. Cool the flask, protecting the contents from dust, transfer the solution to a 50 ml graduated flask and dilute to volume. Measure the optical density of the solution on a Spekker absorptiometer using 4 cm cells and Ilford No. 604 filters (green). The maximum absorption of the solution lies at about 525 nm. The colour is very stable.

Treat the blank solution similarly.

Prepare a calibration curve by treating measured volumes of a standard solution of manganese sulphate exactly as above and plotting the optical densities against the maganese contents of the solutions.

Any other absorptiometer may be used to measure the optical densities but this change may affect the maximum permissible concentration of manganese.

9.3.2 *Method B — With formaldoxime*

9.3.2.1 *Reagents*

a) *Formaldoxime solution* — Dissolve 9 g of analytical reagent quality hydroxylamine hydrochloride in water, add 4·5 ml of 40 percent formaldehyde solution and dilute to 100 ml. The solution is stable for several weeks.

b) *Tartaric acid solution* — 30 g of analytical reagent quality acid in 100 ml.

c) *Cupferron solution* — 10 g of Cupferron in 100 ml of water. Prepare freshly and filter before use.

d) *Saturated bromine water.*

e) *Methyl Orange* — 0·05 percent solution in water.

f) *Zinc cyanide solution* — Dissolve 10 g of analytical reagent quality potassium cyanide in 50 ml of water, and 12 g of analytical reagent quality zinc sulphate ($ZnSO_4.7H_2O$) in 50 ml of water. Mix and add sufficient concentrated ammonium hydroxide to dissolve the precipitate which forms. A small precipitate may form on keeping this solution; decant the supernatant liquid before use.

g) *Methylene chloride* — Recover used solvent by distilling it in presence of about one-tenth its volume of 10 percent sodium hydroxide solution.

h) *Manganous sulphate solution* — Dissolve 2·042 g of manganous sulphate ($MnSO_4.4H_2O$) in water, add 1 ml of concentrated sulphuric acid and dilute to 400 ml. This solution contains approximately 1 mg of manganese per millilitre. Standardize as follows.

Table 3 Effects of Extraneous Ions

(*Clause* 9.2.1)

Extraneous Ion	**Amount** mg	**Periodate (Method A)**	**Formaldoxime (Method B)**
(1)	(2)	(3)	(4)
Aluminium	15	No interference	No interference
Antimonic	150	Interferes (*see* Note 1)	No interference
Borate	100	No interference	Interferes (*see* Note 4)
Calcium	40	No interference	No interference
Chromic	75	Interferes (*see* Note 2)	Interferes (*see* Note 2)
Cobaltous	1	Slight interference (1 mg Co ≡ 2 μg Mn)	Slight interference (1 mg Co ≡ 1·5 μg Mn)
Cupric	35	Slight interference (*see* Note 3)	Slight interference (*see* Note 5)
Ferric	25	Slight interference (*see* Note 3)	No interference*
Lead	15	No interference	No interference
Magnesium	20	No interference	No interference
Mercuric	5	No interference	No interference
Molybdate	500 (Mo)	No interference	No interference
Nickel	1	No interference	No interference
Phosphate	500	No interference	No interference (*see* Note 6)
Sodium	30	No interference	No interference
Stannic	500	Interferes (*see* Note 1)	No interference*
Titanic	40	No interference	No interference*
Tungstate	700 (W)	Interferes (*see* Note 1)	Interferes (*see* Note 1)
Vanadate	300 (V)	Interferes above 10 mg	No interference*
Zinc	80	No interference	No interference
Zirconyl	18	No interference	No interference

*These ions, ferric and vanadate, interfere even at low concentrations, but, they are removed by extraction of their cupferron complexes.

NOTES

1 Tungsten forms a precipitate of tungstic acid that cannot be filtered from the original solution.

Antimony and tin form precipitates when the solution is boiled.

Separate manganese from tungsten by the procedure in Note 2.

Remove antimony and tin by passing hydrogen sulphide into the hot solution (acidity 2N to 3N) until precipitation is complete, filter and evaporate the filterate to a convenient volume before proceeding with the analysis. Quantities of antimony and tin less than 10 mg do not require separation.

2 Chromium forms coloured chromate ions in Method A and coloured tartrate complexes in Method B. It shall be entirely absent for Method A, and only about 1 mg may be present in Method B.

Separate manganese by adding about 3 mg of ferric ion to the dilute sample solution (100 ml) followed by 3 ml of 100 volume hydrogen peroxide and a slight excess of sodium hydroxide solution. Heat the solution to boiling and boil until effervescence cease. Filter hot and wash the precipitate free from chromate. Dissolve the precipitate in dilute sulphuric acid containing 0·1 ml of 5 percent sodium sulphite solution, boil out the excess of sulphur dioxide and determine the manganese by either method.

(*Continued*)

Table 3 Effects of Extraneous Ions — *Contd*

3 Copper and iron interfere by virtue of the colours of their solutions. The absorption of 35 mg of copper is equivalent to about 2 µg of manganese. Separate copper as sulphide (*see* Note 1) or as described in Note 5.

The absorption of 25 mg of iron (*see* **9.3**) is equivalent to about 2 µg of manganese. If much iron is present add 2 ml of phosphoric acid (relative density 1·69) to the sample solution before adding the potassium periodate. The absorption due to the iron will then be negligible.

4 Borate ions react with the formaldoxime. Use 4 ml of a freshly prepared formaldoxime reagent five times as concentrated as that specified if the presence of borate is suspected.

5 The presence of more than about 5 mg of copper tends to cause low recoveries of manganese. Separate the copper by adding excess of sodium diethyldithiocarbamate solution after extracting the iron as described under Method B and continuing to extract with portions of methylene chloride until no further brown colour is removed.

6 Phosphate interferes by producing a precipitates in alkaline solution if appreciable amounts of lead, calcium or magnesium are present. The quantities of these metals or of phosphate normally found in textiles cause no trouble.

Remove lead as sulphate before beginning the analysis.

If calcium is present add sufficient sulphuric acid to the original solution to ensure that the concentration of ammonium salts in the final solution will be 20 percent to 25 percent. This will retain a considerable amount of calcium phosphate in solution.

If magnesium is present, add 2 g of analytical reagent quality sodium pyrophosphate immediately before making the solution alkaline.

Pipette 20 ml of solution into 100 ml of M sulphuric acid, add 1 g of sodium bismuthate, and allow to stand for 5 min with occasional shaking. Filter through a sintered glass (G4) filter or asbestos-padded Gooch crucible, rinse the residue with M sulphuric acid until free from permanganic acid and titrate the filtrate with freshly standardized ferrous sulphate solution: 1 ml 0·1 N reductant ≡ 1·099 mg of Mn. Dilute this solution as required immediately before use.

9.3.2.2 *Procedure*

The procedure allows for the removal of the interfering elements iron, tin, titanium and vanadium by extraction of their Cupferron complexes and for the masking of small quantities of coppor, cobalt and nickel with cyanide. Remove any other interfering elements as detailed in the Notes.

Place the prepared sample solution or an aliquot containing not more than 75 µg of manganese in a seperating funnel. Adjust the volume to about 25 ml and the sulphuric acid content to at least 3 N (the total acidity should not exceed 6 N). Cool if necessary, add 1 ml of Cupferron solution and extract with 10 ml of methylene chloride. Repeat this procedure until the addition of Cupferron produces only a slight precipitate of the free reagent[*], than extract with one further 10 ml portion of methylene chloride[†].

Transfer the aqueous solution to a suitable conical flask, rinsing the funnel with a minimum of water and add 1 ml of 60 percent perchloric acid if the solution does not already contain this acid. Evaporate the solution until fumes of perchloric acid are evolved and all organic matter has been destroyed[*]. Cool, add 20 ml of water, boil for a few minutes to remove chlorine and again cool. Add not more than 0·05 ml of methyl orange solution and 1 ml of tartaric acid solution, and neutralize with concentrated ammonium hydroxide solution.

Add 3 ml of M sulphuric acid and 0·1 ml of bromine water to destry the indicator[†]. Cool, add 2 ml of zinc cyanide solution, 1 ml of formaldoxime solution[‡] and 4 ml of ammonium hydroxide (relative density 0·880). Transfer the solution to a 50 ml graduated flask and dilute to volume. Remove a few millilitres of the solution, shake the remainder vigorously and after an interval of 30 minutes measure the optical density of the solution on a Spekker absorptiometer with 4 cm cells and Ilford No. 602 filters (blue). The maximum absorption of the solution lies at about 460 nm. The colour is stable for at least 4 hours.

Prepare a calibration curve as follows:

Dilute measured amounts of a suitable standard solution of manganous sulphate to about 40 ml. Add 1 ml of tartaric acid 2 ml of zinc cyanide 1 ml of formaldoxime and 3 ml of ammonium hydroxide (relative density 0·880) solution. Measure the optical densities after 30 minutes and plot them against the manganese contents of the solutions.

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[*] The following complexes may be extracted: ferric (brown), molybdate (white), stannic (white), titanic (yellow), vanadate (dark brown), zirconyl (pale yellow). Increase the initial addition of Cupferron until in excess if much metal is present.

[†] If copper is present in quantity proceed as described in Note 5 under Table 3 at this point.

[*] The amount of organic matter remaining is very small and the reaction is without hazard. The organic matter may be destroyed by prolonged digestion with sulphuric acid alone if preferred.

[†] Wide-range indicator paper may be used as external indicator if preferred.

[‡] *See* Note 4 under Table 3.

Any other absorptiometer may be used to measure the optical densities, but this change may alter the maximum permissible concentration of manganese.

10 ESTIMATION OF CHROMIUM (Cr)

10.1 Destruction of the Organic Matter

10.1.1 *Method 1 — Wet Ashing*

This method is preferable to Method 2, particularly when the amount of chromium is small or when siliceous substances or large amounts of other ions are present. The procedure is described in Annex A, but it is essential to use sufficient sulphuric acid to cover the bottom of the flask at all times (*see* Note). The necessary amount is 2 ml for 150 ml flasks and the same amount suffices for 250 ml flasks if the bottoms are truly flat.

At the end of the reaction heat the flask strongly with the neck extension still in place. When the perchloric acid has been expelled the residual acid ceases to boil and changes from yellow-green to colourless. It is not necessary to expel every trace of perchloric acid. Dilute the residue, boil it until free from chlorine, then cool and neutralize it with concentrated ammonium hydroxide solution, methyl orange (0·05 ml of a 0·1 percent solution) being used as an indicator. Re-acidify the solution with 5 ml of 2 N sulphuric acid and adjust it to a final volume of about 30 ml. Prepare a 'blank' by volatilizing nitric and perchloric acids from an appropriate mixture and treating the residual sulphuric acid as described above.

NOTE — The occurrence of bare patches leads to loss of chromium, possibly by volatilization from spray falling on the hot glass.

10.1.2 *Method 2 — Dry Ashing*

This is performed essentially as described in IS 199 : 1989. Determine the mass of the sample in the form of pastilles, place them in a porcelain crucible and impregnate with a 5 percent solution of magnesium nitrate at the rate of 1 ml per gram of the sample. Alcohol may be used to facilitate the impregnation of poorly wettable materials.

Ensure that the inner surface of the crucible has not been damaged or roughened, as this may lead to loss of chromium by combination with the glaze. After ignition, cover the cooled crucible with a watch glass, add 1 ml of concentrated nitric acid and 0·1 g of potassium chlorate and allow the contents to digest on a water-bath until effervescence ceases. Rinse and remove the watch glass and evaporate the contents of the crucible to dryness. Heat the residue on a water bath until it is odourless, dissolve it in 5 ml of 2 N sulphuric acid and dilute to about 30 ml. Prepare a 'blank' by evaporating the appropriate volume of magnesium nitrate solution in a crucible and treating with nitric acid and potassium chlorate as above.

10.2 Removal of Interfering Ions

10.2.1 The effects of other ions on the determination are shown in Table 4. The amounts shown in col 2 are the largest likely to be derived from a 2 g sample of textile material and the expression 'no interference' in col 3 indicates that at least this amount may be tolerated under the conditions detailed in **10.3**. The data relate to wet-ashed samples only; the effects of dry ashing in presence of large amounts of these elements and radicals and of interactions between different ions have not been studied.

Iron and copper cause fading of the colour and variation in its hue; the procedure described in **10.3** therefore provides for the removal of small amounts of these metals.

10.3 Determination

10.3.1 *Reagents*

a) *8-hydroxyquinoline (oxine)* — 1 percent solution in 2 N acetic acid.

b) *Chloroform* — Recover this by shaking it with successive portions of concentrated sulphuric acid until the acid remains almost colourless. Shake the solvent with excess of calcium hydroxide filter and distil it. Add alcohol (1 percent by volume) to the distillate.

c) *Methylene chloride* — Recover the methylene chloride, which is used for the extraction of Cupferron complexes by shaking it with successive portions of a 10 percent solution of sodium hydroxide until the alkali remains almost colourless, and then distilling the solvent over solid sodium hydroxide.

d) *Ceric ammonium sulphate* — 0·05 N solution in 2 N sulphuric acid.

e) *Sodium azide* — 5 percent solution in water.

f) *Diphenylcarbazide* — 0·25 percent solution in equal volumes of acetone and water; this solution must be prepared daily.

g) *Ammonium sulphate* — free from iron and copper. Treat a 20 percent *m/v* solution of the salt with an excess of oxine solution

Table 4 Effects of Extraneous Ions

(*Clause* 10.2.1)

Extraneous Ion (1)	**Amount** mg (2)	**Effect** (3)	**Extraneous Ion** (1)	**Amount** mg (2)	**Effect** (3)
Aluminium	15	No interference	Magnesium	20	No interference
Antimonic	150	Note 1	Manganous	15	Note 4
Borate	100 (H_3BO_3)	No interference	Mercuric	5	Note 1
Calcium	50	No interference	Phosphate	500 (H_3PO_4)	Note 5
Cobaltous	1	No interference	Stannic	500	Note 2
Cupric	35	Note 3	Titanic	40	Note 2
Ferric	25	Note 3	Zinc	80	No interference
Lead	15	No interference even if $PbSO_4$ precipitates	Zirconyl	15 (Zr)	Note 2

NOTES

1 If antimony (ic) and mercury remain in solution they do not interfere, though mercury may cause low results when present during the extraction of traces of iron and copper. It is usually necessary to remove the metals by the following process.

The perchloric acid is not expelled at the end of the wet ashing procedure but the flask is cooled and the residue diluted. The solution is made about 3 N in hydrochloric acid, boiled to dissolve antimonic compounds, if present, and diluted to a total acidity of about 1N. It is then heated on a water-bath for 30 minutes while a current of hydrogen sulphides is passed through it. The flask is than stoppered and cooled. The solution is filtered, the filtrate being returned to the flask and evaporated to small volume. After the neck extension has been replaced on the flask the perchloric acid is expelled and the preparation of the solution completed as in Method 1 (*see* **10.1**).

2 Zirconium, tin and titanium interfere because they are hydrolyzed at low acidities. They may be removed by the following method.

The perchloric acid is not expelled at the end of the wet-ashing procedure but the flask is cooled and the residue diluted. Hydrochloric acid is added, if necessary, to assist the solution of tin and titanium compounds, the solution is boiled until free from chlorine, cooled and diluted until it contains about 10 percent by volume of concentrated acids. It is transferred to a separating funnel, treated with excess of a 10 percent aqueous solution of cupferron, and extracted with several 10 ml portions of methylene chloride. The completeness of the precipitation should be checked by adding more cupferron after the first extraction. The white stannic complex is difficult to distinguish from excess of the reagent but it is less translucent than the latter.

After extraction, the aqueous phase is returned to the flask and evaporated to small volume. The neck extension is replaced, the perchloride acid expelled, and the preparation of the solution completed as in Method 1 (*see* **10.1**).

3 Amounts of iron and copper greater than 1 or 2 mg are not conveniently dealt with by the oxinate extraction procedure described in **10.3**. Large amounts of copper should be separated by the method given in Note 1, and large amounts of iron by that given in Note 2.

If the total amount of iron and copper in the samples is known not to exceed 10 µg the extraction of these metals as their oxinates may be omitted, the neutralized and re-acidified solution being oxidized immediately. Under these circumstances also, the solution from the dry ash may be treated with diphenylcarbazide without further oxidation. The optical densities of the solutions should be read within a few minutes of adding the reagent.

4 Manganese dioxide may be precipitated when the chromium is oxidized and cause low results when more than 1 mg of manganese is present. If the solution is free from ammonium salts as much as 15 mg of manganese may be present.

5 Phosphate causes precipitation of the ceric ion and only 15 mg of phosphoric acid can be tolerated or 5 mg if ammonium salts are absent. By substituting potassium permanganate for ceric ammonium sulphate the full 500 mg of phosphoric acid may be tolerated.

and adjust to pH 5 to 6 (wide range paper) with dilute ammonium hydroxide. Extract the solution with successive portions of chloroform until the solvent remains colourless and then filter it to remove suspended solvent.

10.3.2 *Procedure*

Transfer the acid solution from the ashing process, or an aliquot containing note more than 75 µg of chromium, to a separating funnel, 0·05 ml of a 0·1 percent solution of methyl orange if required, and treat the solution with 1 ml of oxine solution. Neutralize carefully with ammonium hydroxide to the mid hue of the indicator, or until the colour of the indicator is obscured by black ferric oxinate. If the end-point of the indicator is accidentally passed acidify the solution again and repeat the neutralization. Add 10 ml chloroform, shake the funnel vigorously and after the layers have separated, adjust the aqueous layer if necessary to neutrality with ammonia. Again shake the funnel vigorously for 30 seconds*, remove the chloroform layer and extract the aqueous layer twice more with fresh 10 ml portions of chloroform. Return the aqueous layer to the conical flask (*see* Note 3 under Table 4). Acidify the solution with 5 ml of 2 N sulphuric acid, boil to expel any residual chloroform and treat while still boiling with 1 ml of ceric ammonium sulphate solution, boil for a further 10 minutes and cool. Remove any solid, including manganese dioxide, by filtration and treat the clear solution with 0·2 ml of sodium azide solution†. The solution should now be colourless. If the purple colour of permanganate or the brown colour of colloidal manganese dioxide is present warm the solution gently until the colour disappears.

Transfer the cooled solution to 50 ml graduated flask, treat with 2 ml of diphenylcarbazide reagent and dilute to volume. Treat the 'blank' solution, prepared as described in **9.1**, or an aliquot portion corresponding to that used for the actual test exactly as described above.

Shake the solutions vigorously to remove dissolved gases, transfer them to the cells of a Spekker absorptiometer and measure their optical densities with the use of Ilford 605, yellow green filters. Maximum absorption occurs at a wavelength of about 540 nm. The colour is fairly stable but fades to the extent of about 1 percent to 2 percent in 1 hour. Use the difference between the optical densities of the 'test' and 'blank' solutions to obtain the chromium content of the former directly from a calibration graph constructed as follows.

Transfer different measured amounts of a standard solution of potassium dichromate to separate 50 ml volumetric flasks each containing 5 ml of 2 N sulphuric acid and dilute to about 40 ml with water. If acid ashed samples are to be used add 5 g of ammonium sulphate, free from iron and copper. Add 2 ml diphenylcarbazide reagent to each flask, then dilute the contents of each to 50 ml. Plot the optical density of each solution, measured as above, against its chromium content. Make fresh calibration graphs for each batch of solid diphenylcarbazide and check the graphs periodically. Any other absorptiometer may be used, or the solutions may be compared visually with freshly prepared standards in uniform tubes, but these variations may affect the maximum permissible amount of chromium in the sample.

11 ESTIMATION OF ZINC (Zn)

11.1 General

11.1.1 The dithizone method has been adopted for this estimation. According to this method, the test sample is boiled in dilute hydrochloric acid for 30 minutes in an Erlenmeyer flask, the contents cooled, filtered and washed with water, the filtrate and washings yielding a test solution. An aliquot of this solution containing approximately 1 mg of zinc per 100 ml of test solution is treated with acetate buffer solution (pH 4·75) and sodium thiosulphate solution or with potassium cyanide solution and extracted with dithizone to yield a bright red extract. This extract is compared against standard zinc solution treated exactly like the aliquot of the test thiosulphate.

11.1.2 In order to prevent interference due to ions of copper, mercury, lead and cadmium, the procedure provides for the use of sodium thiosulphate solution at pH 4·75. Next to these interfering metallic ions, cobalt and nickel are the other two important metals; when one or both of them are present the estimation has to be repeated and the interference due to one or both of them prevented by the use of potassium cyanide solution in place of sodium thiosulphate.

11.2 Destruction of the Organic Matter

11.2.1 Follow the procedure as described in **7.1.1** or **7.1.2**.

11.3 Reagents

11.3.1 *Acetate Buffer Solution of* p*H 4·75*

Prepared by mixing equal volumes of dilute sodium acetate solution (2 N) and dilute acetic acid (2 N). The solution should be shaken well with 3 or 4 drops of dithizone solution (*see* **11.3.7**) to remove interference due to metallic ions, if any, and filtered through a moistened filter paper to remove drops of carbon tetrachloride.

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*If the combined content of iron and copper exceeds 1 mg, a further 1 ml of oxide should be added and the process repeated until excess oxine is present.

†Hydrazoic acid is very volatile and irritates the mucous membrane. Inhalation of the vapour from these solutions should therefore be avoided.

11.3.2 *Sodium Thiosulphate Solution*

Prepared by dissolving sodium thiosulphate ($Na_2S_2O_3.5H_2O$) in water to yield a 25 percent (*m/v*) solution.

11.3.3 *Dilute Ammonia*

Prepared by diluting ammonia (sp.gr 0·9) in water to yield a 1 : 1 (by volume) solution.

11.3.4 *Potassium Cyanide Solution*

Prepared by dissolving/potassium cyanide in water to yield a 5 percent (*w/v*) solution.

11.3.5 *Dilute Hydrochloric Acid* — approx 2 N.

11.3.6 *Sodium Acetate Solution* — approx 2 N.

11.3.7 *Dithizone Solution*

Prepared by dissolving dithizone $H_5C_6N{=}N{-}C(S)NHNHC_6H_5$ in carbon tetrachloride to yield a 0·001 percent (*m/v*) solution (*see* **7.4.4**).

11.3.8 *Sodium Sulphate* — solid, anhydrous.

11.3.9 *Standard Zinc Solution*

Prepared by dissolving zinc (30 mesh) in dilute hydrochloric acid (0·1 N) to yield a 0·01 percent (*m/v*) solution, taking 10 ml of the solution and diluting with water to exactly 100 ml to yield a 0·001 percent (*m/v*) solution. One millilitre of this solution contains 0·01 mg of zinc (Zn).

11.4 Procedure

11.4.1 From the test solution prepared as in **11.2.1**, choose an aliquot containing approximately 1 mg of zinc per 100 ml of solution (making rough estimations on different known quantities of the test solution, if necessary) transfer (*see also* **11.4.5**) it to a 25 ml separating funnel, add 5 ml of acetate buffer solution and 1 ml of sodium thiosulphate solution (*see* Note); mix with 5 ml of dithizone solution and shake well for 2 minutes. Allow the contents of the separating funnel to settle into two layers and when the lower of the two layers thus formed is free from water droplets, dry the stem of the funnel with a piece of filter paper rolled round a thin glass rod and run the lower layer (extract) into a 25-ml volumetric flask, avoiding exposure to direct sunlight. Keep the flask well stoppered.

NOTE — When appreciable amounts of cobalt or nickel or both are present, add instead of acetate buffer and sodium thiosulphate solutions, enough ammonia to neutralize and enough potassium cyanide solution to dissolve the precipitate first formed; then add dilute hydrochloric acid drop by drop to bring the *p*H between 3 and 4 and adjust the *p*H to 5 to 5·5 with the addition of sodium acetate solution. Use standard *p*H papers for adjusting *p*H.

11.4.2 Re-extract the portion left in the funnel with 2 or 3 ml of carbon tetrachloride and shake well for 2 minutes. Allow the contents of the funnel to settle again into two layers and when the lower of the two layers now formed is free from water droplets, dry the stem of the funnel with a piece of filter paper rolled round a tin glass rod and run the lower layer into the 25 ml volumetric flask containing the extract obtained as in **11.4.1**.

11.4.3 Repeat the extraction two or three times (or until the aqueous layer in the separating funnel is free from red colour) collecting all the extracts in the same volumetric flask.

11.4.4 Dilute the total extract with carbon tetrachloride to exactly 25 ml; add 1 g of sodium sulphate and shake well.

11.4.5 Prepare a series of reference standards taking different known quantities of standard zinc solution contain approximately 1 mg or less of zinc per 100 ml of solution and treating the solutions side by side with and exactly as the aliquot of the test solution (*see* **11.4.1** to **11.4.4**).

11.4.6 Treat the 'blank' solution or an aliquot portion corresponding to that used for the actual determination exactly as described from **11.4.1** to **11.4.5**.

11.4.7 Measure the optical densities of the extracts at suitable wavelength where the absorption of the unchanged dithizone is at a minimum (510 nm). The difference between the optical densities of the 'test' and 'blank' extracts is used to obtain the zinc content directly from a calibration graph constructed as given in **11.4.8**.

11.4.8 Extract a series of solutions containing different measured amounts of standard zinc solutions and measure the optical densities of the extracts. Substract from each value the optical density of the extract from a similar solution containing no added zinc and plot the differences against the zinc contents of the original solutions. These differences are substantially independent of the concentration of the dithizone solution with in the range 0·001 5 percent to 0·002 5 percent.

NOTES

1 The success of this method depends on scrupulous cleanliness. All apparatus shall be washed, first with dilute hydrochloric acid and then with distilled water immediately before use.

2 The colour of the extract and those of extracts prepared similarly from a series of aqueous solutions containing known amounts of zinc may be compared visually in small stoppered tubes of uniform dimensions. The colours are stable for a few hours if the solutions are protected from light.

12 REPORT

12.1 The report shall include the following information:

a) Type and nature of textile being tested;

b) Amounts of copper, iron, manganese, chromium or zinc present; and

c) The type of treatment, if given to the fabric.

ANNEX A

(*Clauses* 7.1.1, 9.1.1 *and* 10.1.1)

WET ASHING OF TEXTILE MATERIALS

A-1 INTRODUCTION

A-1.1 Where destruction of organic matter in a sample of textile material is required, and the ash is not to be determined, wet ashing possesses many advantages over dry ashing.

A-2 PRECAUTIONARY NOTE

A-2.1 To avoid hazard, the conditions described must be carefully followed and any variation or extension of the method to materials other than those mentioned must be made only by fully trained operators.

A-3 PRINCIPLE

A-3.1 This method involves the controlled heating of the sample with a suitable mixture of nitric, sulphuric and perchloric acids.

A-4 APPARATUS AND REAGENTS

A-4.1 *Conical Flasks* — with neck extensions (*see* Note 1).

A-4.2 *Hot Plate* — with provision for maintaining graded surface temperatures.

A-4.3 *Safety Glass Screen* — advisable until the operator has had some experience of the method, and essential when working with previously untried materials.

A-4.4 *Boiling Rods*

A-4.5 *Nitric Acid* — concentrated, relative density 1·42.

A-4.6 *Sulphuric Acid* — concentrated, relative density 1·84.

A-4.7 *Perchloric Acid* — 60 percent, relative density 1·54 (*see* Note 2).

A-5 PROCEDURE

A-5.1 Place the specimen in the flask and add in the above order the requisite quantities of the three acids. After each addition, swirl the flask and allow any reaction which takes place to proceed to completion before making a further addition. Fit a neck extension to the flask, which is then placed on the cooler side of the hot plate, housed in an efficient fume cupboard. Vigorous evolution of brown fumes occurs, accompanied by partial or complete solution of the sample. Cotton dissolves only slowly, and most coating materials are resistant to oxidation at this stage.

A-5.2 When the evolution of brown fumes has slackened, move the flask to the middle of the plate and allow excess of nitric acid and water to boil off gently. A gradually increasing evolution of gas, culminating in a vigorous reaction and generation of heavy white fumes, marks the action of the perchloric acid and the virtual completion of the oxidation. The reaction may be moderated, if necessary, by sliding the flask back to the cooler side of the hot plate. Charring of the reaction mixture at any stage should be rectified by swirling the flask or by adding a few drops of concentrated nitric acid.

A-5.3 Finally, move the flask to the hottest part of the plate and allow the residual acid to reflux until the walls of the flask and the lower portion of the neck have been thoroughly washed by the distillate. During this process, lift the neck extension momentarily about three times to release liquid held by capillary attraction at the junction with the flask.

A-5.4 After the flask has been cooled, rinse the neck extension with about 20 ml of water and remove it. Then boil the acids, thus diluted, for 2 minutes to expel chlorine, using a boiling rod to prevent bumping. The diluted perchloric acid possess no oxidizing properties and the solution at this stage is ready for analysis.

A-5.5 Table 1 shows the amounts of each acid recommended. The quantities given are suitable for use in 250 ml flasks unless otherwise stated. The addition of sulphuric acid produces a smoother reaction and facilitates the clearance of any charring that may occur. When the nature of the subsequent analysis renders its presence undesirable it may be replaced by an equal volume of perchloric acid, except in the few instances indicated.

NOTES

1 Conical flasks of 250 ml capacity are suitable for most purposes. The neck extensions are easily made by drawing down the closed ends of 200 mm × 25 mm boiling tubes, blowing out the ends, chamfering them with a wire gauze and then flame polishing. Extensions for flasks of other sizes are made from tubes of proportionate dimensions.

2 The perchloric acid is pure enough for all but trace analysis, for which purpose it may be purified easily and economically by distillation as the 72 percent azeotrope under reduced pressure.

3 The safety of the reaction depends upon the fact that readily oxidizable matter destroyed by the nitric acid before the perchloric acid reaches its reaction temperature of about 140°C. Addition of the acids in the order given reduces the risk of accidental ommission of the nitric acid.

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